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(54) Method for surface treatment of carbon fibers.

(57) The present invention provides a method for surface treatment of carbon fibers which comprises allowing an alkali metal nitrate to adhere to carbon fibers in an amount of 0.01-5% by weight based on the weight of the carbon fibers and then heat treating the carbon fibers in the air at a temperature between at least the melting point or at least the decomposition temperature of the alkali metal nitrate and lower than 500 °C.

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BACKGROUND OF THE INVENTION

The present invention relates to a method for surface treating carbon fibers and in particular, to a method for surface treating carbon fibers by thermal oxidation which are used for improving strength of moldings made from carbon fiber-reinforced composite materials.

It is well known that carbon fibers are used as reinforcing materials for fiber-reinforced composite materials, especially, fiber-reinforced resins because of their many excellent properties as industrial materials such as heat resistance, endurance, chemical resistance, lightness in weight, high modulus and small thermal expansion coefficient.

On the other hand, carbon fibers have the characteristic that compatibility with resins decreases with increase in the modulus. Therefore, there appears the defect that when fiber-reinforced resins are made by using carbon fibers of high modulus as they are, the resins decrease in shearing force.

In order to remove this defect, a method has been developed which aims at improving compatibility with resins by subjecting the surface of carbon fibers to some treatments.

The main surface treatments are oxidation treatments and at present there are chemical oxidation, electrolytic oxidation and vapor phase oxidation.

The chemical oxidation and the electrolytic oxidation are concisely explained in Sugio Otani, Kensuke Okuda and Shigeru Matsuda, "Carbon Fibers", (published on June 15, 1972 and reprinted with additions and emendations from Kindai Henshusha K.K., ISBN 4-87403-002-5 C3043), pages 217-222.

With reference to the chemical oxidation, this is not suitable for industrialization in view of the long time required for treatment and the small throughput per one operation together with the problem in safety in using nitric acid of high concentrations, although there are no problems in observing and measuring progress of oxidation of the surface of carbon fibers in a laboratory.

The electrolytic oxidation is sometimes employed for surface treatment of long carbon fibers. However, in comparison with loss in weight due to the oxidation, introduction of acidic group into the surface of carbon fibers is not sufficient and moreover, there is the problem that a large amount of waste liquors containing graphitic acid remain after electrolysis. Besides, this method which is effective for long fibers cannot substantially be applied to the surface treatment of short fibers because the short carbon fibers are difficult to use as an electrode. Thus, there are many limitations for employment of this method.

The air oxidation is a representative of the vapor phase oxidation. As the surface treatment of carbon fibers, the air oxidation is the simplest and is easy for industrial employment. However, when this method is used for surface treatment of pitch carbon fibers, the oxidation temperature reaches about 500°C for treatment of carbon fibers of high modulus made from mesophase pitches prepared from petroleum asphalt or coal tar or mesophase pitches obtained by polymerization of condensed polycyclic hydrocarbons produced by the processes described in Japanese Patent Kokai (Laid-Open) Nos. 1-139621 and 1-254796 or substances containing the condensed polycyclic hydrocarbons, namely, so-called aromatic resins (AR). Accordingly, this method is also not suitable for practical use. Furthermore, when the temperature reaches the above range, oxidative destruction of carbon fibers progresses in the air and strength per se of the fibers reduces.

Furthermore, even if the air as an oxidizing gas is replaced with a gas of high oxygen content, the oxidizing efficiency does not increase so much and when ozone is added to the oxidizing gas or the oxidizing gas is irradiated with ultraviolet rays for enhancing oxidizing efficiency, the working atmosphere is endangered and these means cannot be industrially employed.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a method for thermal oxidation of carbon fibers according to which the carbon fibers can be efficiently surface treated to a proper extent with lowering the treating temperature and shortening the treating time irrespective of the kind of starting materials (polyacrylonitriles, pitches or any other materials) and the shape (long fibers and short fibers).

As a result of the intensive research conducted by the inventors for solving the above problems, it has been found that temperature for oxidation of carbon fibers can be lowered and oxidizing rate can be increased by applying an alkali metal nitrate to carbon fibers and then oxidizing the carbon fibers in the air at a temperature in a proper range. Thus, the present invention has been accomplished.

That is, the present invention is a method for surface treatment of carbon fibers, characterized by allowing an alkali metal nitrate to adhere to carbon fibers in an amount of 0.01-5% by weight based on the weight of the carbon fibers and then heat treating the carbon fibers in the air at a temperature of the melting point or higher of the alkali metal nitrate and lower than 500°C. Preferably, the present invention is a

method for surface treatment of carbon fibers, characterized by allowing an alkali metal nitrate to adhere to carbon fibers in an amount of 0.01-5% by weight based on the weight of the carbon fibers and then heat treating the carbon fibers in the air at a temperature of the decomposition temperature or higher of the alkali metal nitrate and lower than 500 °C.

DESCRIPTION OF THE INVENTION

The method for surface treatment of the present invention will be explained in detail.

The carbon fibers to be treated have no special limitation. The carbon fibers may be any of those which are prepared from polyacrylonitriles, pitches, rayons and other starting materials. Further, they may be of any shapes such as long fibers, short fibers, milled fibers and others and besides, they may have rising whiskers on the surface. The method of the present invention can be applied to carbon fibers having any mechanical characteristics, namely, any of general-purpose carbon fibers, high-strength carbon fibers, high-modulus carbon fibers and others. However, since this method is high in treating efficiency, it is preferably applied to the high-modulus carbon fibers which are generally difficult to oxidize the surface, for example, mesophase carbon fibers and aromatic pitch carbon fibers.

The alkali metal nitrate used in the present invention includes sodium nitrate, potassium nitrate and rubidium nitrate. Of these nitrates, preferred is potassium nitrate which has no deliquescence and is easily available as industrial materials.

These alkali metal nitrates are used preferably as an aqueous solution of 0.05-10% by weight in concentration or as fine powders of 0.1-5 μ m in particle size.

The method of allowing the alkali metal nitrate to adhere to carbon fibers includes, for example, impregnating the carbon fibers with an aqueous solution of the nitrate, spraying an aqueous solution of the nitrate or fine powders of the nitrate onto the carbon fibers, sprinkling fine powders of the nitrate on the carbon fibers or dusting the carbon fibers with fine powders of the nitrate. The adhering amount of the alkali metal nitrate to carbon fibers is calculated from amount of the aqueous solution retained by the carbon fibers (pickup) and concentration of the aqueous solution when the alkali metal nitrate is used as an aqueous solution.

The alkali metal nitrate is allowed to adhere to carbon fibers in an amount of 0.01-5% by weight, preferably 0.03-3% by weight based on the weight of the carbon fibers by the above-exemplified method and then, the carbon fibers are heated in the air to carry out oxidation. If the adhering amount of the alkali metal nitrate is less than 0.01% by weight, the effect of using the alkali metal nitrate in the oxidation treatment cannot be obtained and if it is more than 5% by weight, a long time is required for removal of the alkali metal nitrate by washing after the oxidation treatment or the remaining alkali metal nitrate causes deterioration of resins which become a matrix for carbon fibers.

In the oxidation treatment, predrying is not necessarily essential even in the case of impregnation with aqueous solution and the oxidation can be started for the wet carbon fibers as they are.

The heating temperature is at lowest the melting point, preferably at lowest the decomposition temperature of the alkali metal nitrate and lower than 500 °C.

The heating temperature is set in the above range because the surface treating method of the present invention utilizes oxygen generated when the alkali metal nitrate is subjected to heat decomposition. When the alkali metal nitrate is heat decomposed, oxygen and an alkali metal nitrite are produced. The oxygen which is locally generated on the surface of carbon fibers makes it possible to perform rapid oxidation at a temperature lower than in conventional methods. Therefore, if the heating temperature for the oxidation treatment is higher than 500 °C as in the usual air oxidation, the carbon fibers are excessively oxidized and the modulus is damaged or the use of the alkali metal nitrate becomes meaningless.

On the other hand, when the treatment is effected at a temperature lower than the melting point of the alkali metal nitrate, generation of oxygen due to heat decomposition does not occur and hence, the surface treatment cannot be effectively carried out.

Melting points and decomposition temperatures of the alkali metal nitrates used in the present invention are shown below.

	Melting point	Decomposition temperature
(a) Sodium nitrate (NaNO_3)	306.8 °C	380 °C
(b) Potassium nitrate (KNO_3)	333 °C	about 400 °C
(c) Rubidium nitrate (RbNO_3)	310 °C	at least 310 °C

The treating time varies depending on various conditions of the kind and the amount of the alkali metal nitrates used and whether the carbon fibers to be treated are polyacrylonitrile type or pitch type, whether long fibers or short fibers and whether general-purpose carbon fibers, high-strength carbon fibers or high-modulus carbon fibers. In general, suitable range is 10-120 minutes. A range of 10-60 minutes is especially suitable when pitch type short fibers are treated with potassium nitrate.

After the above oxidation treatment, if necessary, the carbon fibers are washed with water.

Mere idea of using nitrates for vapor phase oxidation of carbon fibers is shown in Japanese Patent Kokai (Laid-Open) No.52-25199 and U.S. Patent No.3876444.

However, the nitrates used in Japanese Patent Kokai (Laid-Open) No.52-25199 are salts of copper, silver, zinc, cadmium, tin, lead, vanadium, antimony, bismuth, chromium, molybdenum, tungsten and the like and the treating temperature is low, namely, 80-120°C and thus, the technique of this publication is utterly different from the present invention. U.S. Patent No.3876444 also discloses a surface treating method for carbon fibers with formates, acetates or nitrates of copper, lead, cobalt or cadmium and vanadium pentoxide in combination by vapor phase oxidation. Like the invention of Japanese Patent Kokai (Laid-Open) No.52-25199, this method also utilizes the catalytic action possessed by nitrates of heavy metals and is different in action and mechanism from the surface treating method of the present invention which uses alkali metal nitrates.

In the surface treating method of the present invention, the excellent oxidizing ability is due to the fact that when an alkali metal nitrate is placed in an atmosphere of at least the melting point, preferably at least the decomposition temperature of the alkali metal nitrate, the nitrate decomposes into oxygen and a nitrite. The oxygen generated at the decomposition is in nascent state and rapidly oxidizes the carbon fibers at a treating temperature of 310-5007°C. Therefore, oxidative surface treatment of carbon fibers can be performed at a lower temperature and a higher speed than utilizing the catalytic action of activating the oxygen in the air (oxidizing gas) with nitrate ion as in the above prior art.

The idea of using potassium nitrate for surface treatment of carbon fibers is shown in Popovska et al, "Carbon", Vol.23, No.6, 675-679 (1985). However, the treating temperature employed by them is 600-800°C, which is too high and hence, the treatment can be properly performed in nitrogen, but becomes excessive in the air to damage the modulus of the treated carbon fibers and that of reinforced resins obtained using the treated carbon fibers. Moreover, the conditions of 600-800°C in nitrogen cannot be industrially employed for the treatment such as the surface treatment of carbon fibers and the merit of using alkali metal nitrates for the surface treatment cannot be utilized under such conditions from the aspect of the present invention.

The following nonlimiting examples explain the present invention in more detail.

Preparation Example 1 Preparation of mesophase pitch carbon fibers

A precursor pitch containing 90% of mesophase which was prepared from coal pitches was melt spun at 340°C to obtain pitch fiber strands. The strands of the pitch fibers were cut to 3 mm in length and heated to 310°C at a rate of 1°C/min in the air atmosphere to infusibilize them. The infusibilized strands were further heated to 1000°C at a rate of 5°C/min in the nitrogen atmosphere and kept at that temperature for 10 minutes to make carbon fiber chopped strands.

Preparation Example 2 Preparation of aromatic resin carbon fibers

AR (aromatic resin manufactured by Mitsubishi Gas Chemical Company, Inc.) having a softening point of 240°C as a precursor was melt spun at 330°C to obtain AR pitch fiber strands. The strands of the pitch fibers were cut to 3 mm in length and heated to 270°C at a rate of 1°C/min in the air atmosphere to infusibilize them. The infusibilized strands were further heated to 1000°C at a rate of 5°C/min in the nitrogen atmosphere and kept at that temperature for 10 minutes to make carbon fiber chopped strands.

Example 1 Oxidation treatment of mesophase pitch carbon fibers

The carbon fiber chopped strands obtained in Preparation Example 1 were dipped in a 0.1% aqueous potassium nitrate solution and then taken out. In this case, pickup of the 0.1% aqueous potassium nitrate solution retained by the chopped strands was 30%. The chopped strands were dried at 120°C to allow potassium nitrate to adhere to the surface of the carbon fibers. In this case, adhering amount of potassium nitrate was 0.03%.

The chopped strands containing potassium nitrate adhering to the surface of the carbon fibers were heat treated at 425 °C for 30 minutes.

Example 2 Oxidation treatment of mesophase pitch carbon fibers

In the same manner as in Example 1, potassium nitrate was allowed to adhere to the carbon fiber chopped strands obtained in Preparation Example 1. Then, the carbon fiber chopped strands were heat treated in the same manner as in Example 1 except that the heat treating temperature was 450 °C.

Example 3 Oxidation treatment of mesophase pitch carbon fibers

In the same manner as in Example 1, potassium nitrate was allowed to adhere to the carbon fiber chopped strands obtained in Preparation Example 1. Then, the carbon fiber chopped strands were heat treated in the same manner as in Example 1 except that the heat treating temperature was 475 °C.

Reference Example 1 Measurement of flexural strength of composite material made of mesophase pitch carbon fibers subjected to oxidation treatment and nylon 6

The carbon fiber chopped strands obtained by heat treatment in Examples 1-3 were dipped in a polyether type urethane resin emulsion (solid content 1% by weight) to sufficiently impregnate the chopped strands with the emulsion and then dried at 120 °C to size the chopped strands.

Then, in order to confirm the effect of the surface treatment, a composite molding was made of a thermoplastic resin and the above chopped strands and flexural strength thereof was measured.

That is, 70 parts by weight of nylon 6 (manufactured by Toyobo Co., Ltd.) and 30 parts of the chopped strands of the above Examples 1-3 were blended and made into a compound using a single-screw extruder at 265 °C. This compound was molded into a test piece of 126 mm in length, 12 mm in width and 6 mm in thickness by an injection molding machine under the conditions of cylinder temperature: 270 °C and mold temperature: 90 °C.

Flexural strength of the resulting test piece was measured in accordance with ASTM D790. The results are shown in Table 1.

Table 1

Sample	Oxidizing temperature (°C)	Flexural strength (kg/cm ²)
Example 1	425	2370
Example 2	450	2407
Example 3	475	2405

Comparative Reference Example 1

Measurement of flexural strength of composite material made of mesophase pitch carbon fibers subjected to no oxidation treatment and nylon 6

A molding was made in the same manner as in Reference Example 1 except that the unoxidized carbon fiber chopped strands prepared in Preparation Example 1 were used and flexural modulus of the molding was measured in the same manner as in Reference Example 1 to obtain 2295 kg/cm².

Example 4 Oxidation treatment of aromatic resin carbon fibers

The carbon fiber chopped strands obtained in Preparation Example 2 were dipped in a 0.05% aqueous potassium nitrate solution and then taken out. In this case, pickup of the 0.05% aqueous potassium nitrate solution retained by the chopped strands was 30%. The chopped strands were dried at 120 °C to allow potassium nitrate to adhere to the surface of the carbon fibers. In this case, adhering amount of potassium nitrate was 0.015%.

The chopped strands containing potassium nitrate adhering to the surface of the carbon fibers were heat treated at 425 °C for 30 minutes in a muffle furnace.

Example 5 Oxidation treatment of aromatic resin carbon fibers

In the same manner as in Example 4, potassium nitrate was allowed to adhere to the carbon fiber chopped strands obtained in Preparation Example 2 using 0.1% aqueous potassium nitrate solution. Adhering amount of potassium nitrate in this case was 0.03%. The heat treatment was conducted in the same manner as in Example 4.

Example 6 Oxidation treatment of aromatic resin carbon fibers

In the same manner as in Example 4, potassium nitrate was allowed to adhere to the carbon fiber chopped strands obtained in Preparation Example 2 using 0.3% aqueous potassium nitrate solution. Adhering amount of potassium nitrate in this case was 0.09%. The heat treatment was conducted in the same manner as in Example 4 except that the heating temperature was 400 °C.

Example 7 Oxidation treatment of aromatic resin carbon fibers

In the same manner as in Example 4, potassium nitrate was allowed to adhere to the carbon fiber chopped strands obtained in Preparation Example 2 using 0.3% aqueous potassium nitrate solution. Adhering amount of potassium nitrate in this case was 0.09%. The heat treatment was conducted in the same manner as in Example 4 except that the heating temperature was 375 °C.

Example 8 Oxidation treatment of aromatic resin carbon fibers

In the same manner as in Example 4, potassium nitrate was allowed to adhere to the carbon fiber chopped strands obtained in Preparation Example 2 using 0.5% aqueous potassium nitrate solution. Adhering amount of potassium nitrate in this case was 0.15%. The heat treatment was conducted in the same manner as in Example 4.

Example 9 Oxidation treatment of aromatic resin carbon fibers

In the same manner as in Example 4, potassium nitrate was allowed to adhere to the carbon fiber chopped strands obtained in Preparation Example 2 using 1.0% aqueous potassium nitrate solution. Adhering amount of potassium nitrate in this case was 0.30%. The heat treatment was conducted in the same manner as in Example 4.

Example 10 Oxidation treatment of aromatic resin carbon fibers

The carbon fiber chopped strands obtained in Preparation Example 2 were dipped in a 10% aqueous potassium nitrate solution and then taken out. In this case, pickup of the 10% aqueous potassium nitrate solution retained by the chopped strands was 28%. The chopped strands were dried at 120 °C to allow potassium nitrate to adhere to the surface of the carbon fibers. In this case, adhering amount of potassium nitrate was 2.8%.

The chopped strands containing potassium nitrate adhering to the surface of the carbon fibers were heat treated at 425 °C for 10 minutes.

Comparative Example 1 Air oxidation of aromatic resin carbon fibers

The carbon fiber chopped strands obtained in Preparation Example 2 were heat treated in the air at 530 °C for 60 minutes to perform surface oxidation of the carbon fibers.

Reference Example 2 Measurement of flexural strength of composite material made of aromatic resin carbon fibers subjected to oxidation treatment and polycarbonate resin

The carbon fiber chopped strands obtained by heat treatment in Examples 4-10 were dipped in a bisphenol type epoxy resin emulsion (solid content 1% by weight) to sufficiently impregnate the chopped strands with the emulsion and then sufficiently dried to size the chopped strands.

Then, in order to confirm the effect of the surface treatment, a composite molding was made of a thermoplastic resin and the above chopped strands and flexural strength thereof was measured.

That is, 80 parts by weight of EUPYRON S-2000 (polycarbonate resin manufactured by Mitsubishi Gas Chemical Company, Inc.) and 20 parts of the chopped strands of the above Examples 4-9 were blended and made into a compound using a single-screw extruder at 300 °C. This compound was molded into a test piece of 126 mm in length, 12 mm in width and 6 mm in thickness by an injection molding machine under the conditions of cylinder temperature: 300 °C and mold temperature: 120 °C.

Flexural strength of the resulting test piece was measured in accordance with ASTM D790. The results are shown in Table 2.

Table 2

Sample	Adhering amount of KNO ₃ (%)	Oxidizing temperature (°C)	Treating time (min)	Flexural strength of molding (kg/cm ²)
Example 4	0.015	425	30	1777
Example 5	0.03	425	30	1754
Example 6	0.09	400	30	1850
Example 7	0.09	375	30	1654
Example 8	0.15	425	30	1821
Example 9	0.3	425	30	1641
Example 10	2.8	425	10	1735

Comparative Reference Example 2

Measurement of flexural strength of composite material made of aromatic resin carbon fibers subjected to no oxidation treatment and aromatic resin carbon fibers subjected to air oxidation and polycarbonate

A molding was made in the same manner as in Reference Example 2 except that the unoxidized carbon fiber chopped strands prepared in Preparation Example 2 or those of Comparative Example 1 were used and flexural strength thereof was measured in the same manner as in Reference Example 2. The results are shown in Table 3.

Table 3

Sample	Oxidizing temperature (°C)	Treating time (min)	Flexural strength of molding (kg/cm ²)
Unoxidized	-	-	1573
Comparative Example 1	530	60	1630

Example 11 Oxidation treatment of mesophase pitch carbon fibers

The carbon fiber chopped strands obtained in Preparation Example 1 were dipped in a 0.5% aqueous potassium nitrate solution and then taken out. In this case, pickup of the 0.5% aqueous potassium nitrate solution retained by the chopped strands was 30%. The chopped strands were dried at 120 °C to allow potassium nitrate to adhere to the surface of the carbon fibers. In this case, adhering amount of potassium nitrate was 0.15%.

The chopped strands containing potassium nitrate adhering to the surface of the carbon fibers were heat treated at 400 °C for 60 minutes.

Comparative Example 2 Air oxidation of mesophase pitch carbon fibers

The carbon fiber chopped strands obtained in Preparation Example 1 were heat treated in the air at 470 °C for 60 minutes to perform surface oxidation of the carbon fibers.

Reference Example 3 Measurement of flexural strength of composite material made of mesophase pitch carbon fibers subjected to oxidation treatment and polyacetal resin

The carbon fiber chopped strands obtained by heat treatment in Example 11 were dipped in a polyether type urethane resin emulsion (solid content 1% by weight) to sufficiently impregnate the chopped strands with the emulsion and then sufficiently dried to size the chopped strands.

Then, in order to confirm the effect of the surface treatment, a composite molding was made of a thermoplastic resin and the above chopped strands and flexural strength thereof was measured.

That is, 80 parts by weight of DURACON (polyacetal resin manufactured by Polyplastics Co., Ltd.) and 20 parts by weight of the chopped strands of the above Examples 11 were blended and made into a compound using a single-screw extruder at 200 °C. This compound was molded into a test piece of 128 mm in length, 12 mm in width and 6 mm in thickness by an injection molding machine under the conditions of cylinder temperature: 200 °C and mold temperature: 90 °C.

Flexural strength of the resulting test piece was measured in accordance with ASTM D790. The flexural strength of the molding is 1848 kg/cm².

Comparative Reference Example 3

Measurement of flexural strength of composite material made of mesophase pitch carbon fibers subjected to no oxidation treatment and mesophase pitch carbon fibers subjected to air oxidation and polyacetal resin

A molding was made in the same manner as in Reference Example 3 except that the unoxidized carbon fiber chopped strands prepared in Preparation Example 1 or those of Comparative Example 2 were used and flexural strength thereof was measured in the same manner as in Reference Example 3. The results are shown in Table 4.

Table 4

Sample	Oxidizing temperature (°C)	Treating time (min)	Flexural strength of molding (kg/cm ²)
Unoxidized	-	-	1735
Comparative Example 2	470	60	1744

According to the present invention, all sorts of carbon fibers including high-modulus carbon fibers the oxidation of the surface of which have been difficult can be properly surface treated at a lower treating temperature and in a shorter treating time than in conventional methods without damaging the modulus of carbon fibers.

Thus, it becomes possible to provide carbon fiber-reinforced resin composite materials maintaining the modulus of the carbon fibers and excellent in shearing force.

Claims

1. A method for surface treatment of carbon fibers which comprises allowing an alkali metal nitrate to adhere to carbon fibers in an amount of 0.01-5% by weight based on the weight of the carbon fibers and then heat treating the carbon fibers in the air at a temperature between at least the melting point of the alkali metal nitrate and lower than 500 °C.
2. A method for surface treatment of carbon fibers which comprises allowing an alkali metal nitrate to adhere to carbon fibers in an amount of 0.01-5% by weight based on the weight of the carbon fibers and then heat treating the carbon fibers in the air at a temperature between at least the decomposition temperature of the alkali metal nitrate and lower than 500 °C.
3. A method according to claim 1 or 2, wherein the alkali metal nitrate is sodium nitrate, potassium nitrate or rubidium nitrate.
4. A method according to claim 3, wherein the alkali metal nitrate is potassium nitrate.

5. A method according to claim 1 or 2, wherein the carbon fibers are mesophase pitch fibers or aromatic pitch carbon fibers.
6. A method according to claim 1 or 2, wherein the heat treating time is 10-120 minutes.
7. A method according to claim 1 or 2, wherein the alkali metal nitrate is used in the form of an aqueous solution or fine powders.

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EUROPEAN SEARCH REPORT

Application Number

EP 93 10 0330

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-3 627 570 (CASS ET AL) * the whole document *	1-3,7	D01F11/12
X	EP-A-0 267 995 (TOA NENRYO K.K.K.) * the whole document *	1-3,7	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D01F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 01 MARCH 1993	Examiner HELLEMANS W.J.R.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons A : member of the same patent family, corresponding document	

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